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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 3 :		(11) International Publication Number:
D21C 9/10	A1	WO 84/ 00181
		(43) International Publication Date: 19 January 1984 (19.01.84)

(21) International Application Number: PCT/US83/00820

(22) International Filing Date: 1 June 1983 (01.06.83)

(31) Priority Application Number: 391,747

(32) Priority Date: 24 June 1982 (24.06.82)

(33) Priority Country: US

(71) Applicant: SCOTT PAPER COMPANY [US/US]; Industrial Highway at Tinicum Island Road, Philadelphia, PA 19113 (US).

(72) Inventor: SINGH, Rudra, P. ; 4404 Chandler Drive, Brookhaven, PA 19015 (US).

(74) Agent: WEYGANDT, John, A.; Scott Plaza II, Philadelphia, PA 19113 (US).

(81) Designated States: AU, FI, FR (European patent), GB (European patent), JP, SE (European patent).

Published
With international search report.

(54) Title: OZONE BLEACHING OF CELLULOSIC MATERIALS

(57) Abstract

In a process for bleaching lignocellulosic pulp with ozone, irradiation of the pulp with ultraviolet light enhances the efficiency of the ozone and the bleachability of the pulp.

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OZONE BLEACHING OF CELLULOSIC MATERIALS

BACKGROUND OF THE INVENTION

Field of the Invention

Bleaching lignocellulosic material with ozone.

BRIEF SUMMARY OF THE INVENTION

It has been found that, during pulp bleaching with ozone, irradiation of the pulp with ultraviolet light enhances the efficiency of the ozone and the bleachability of the pulp.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The following definitions will be used in this application.

Pulping is the changing of wood chips or other lignocellulosic material to fibrous form. Chemical pulping requires cooking of such material in solution with a chemical, and includes partial removal of the coloring matter such as lignin associated with the wood.

Bleaching is the treatment of cellulosic fibers to remove or alter the coloring matter associated with the fibers to allow the fiber to reflect white light more truly.

The present invention is concerned with the degradation of lignin and hence "delignification" and "bleaching" are used interchangeably.

Consistency is the weight of pulp fibers in a pulp suspension usually expressed as a percentage. For example, one pound oven dry fiber in one hundred pounds of a mixture of water and fibers would be a pulp suspension of 1% consistency. The consistency of the pulp will depend upon the type of dewatering equipment used.

The following definitions of consistency are based on the use of those terms in "The Bleaching of Pulp," Third Edition, Revised, edited by the present inventor, TAPPI Press 1979, pages 243-46.

Low consistency is typically from 4-6%. It is a suspension that is pumpable in an ordinary centrifugal pump and is obtainable using deckers and filters without press rolls.

Medium consistency is between 10 and 15%. This consistency can be obtained by vacuum washers and vacuum thickeners. Above 15%, press rolls are needed for dewatering. A medium consistency slurry is pumpable by special machinery.

High consistency is from 20-35%. This consistency is obtained by the use of presses. High consistency pulp is essentially nonpumpable.

One measure of the efficacy of a bleaching process is the degree of delignification. There are many methods of measuring the degree of delignification of the pulp, but most are variations of the permanganate test.

The permanganate test used herein provides a Kappa number--a measure of potassium permanganate solution consumed by oven dry pulp under specified conditions. The Kappa number is determined in accordance with TAPPI standard test method T 214 M42.

A fairly lengthy recitation of prior art literature and patent references describing gas phase ozone bleaching of lignocellulosic materials is contained in U.S. Patent 4,080,249 to Kempf et al column 1, lines 31-46. These references disclose the ozone bleaching of pulp at low, medium and high consistencies. Therefore, "ozone bleaching" as used herein is not to be limited to any particular consistency but may be employed at whatever consistency is preferred, as suitable apparatus is already known for all three levels. For low and medium consistency pulp, i.e. pumpable slurries, a photoreactor such as disclosed for example in U.S. Patent 3,637,342 to Veloz can be employed, following the teachings of Kempf et al for entraining the ozone bearing gas into the slurry of pulp. For high consistency pulp reactors, such as disclosed by Fritzvold in U.S. Patents 4,278,496 and 4,123,317 and by Carlsmith in U.S. Patents 3,814,664 and 3,964,962 it is contemplated that lamps emitting ultraviolet light be mounted on the walls of the reaction chamber.

In accordance with the present invention, ultraviolet radiation increases the effectiveness of the ozonation. Without wishing to be bound by theory, the present inventor believes that the ultraviolet radiation electronically excites the lignin in the material to be bleached. The excited lignin may then form a high energy complex with the ozone (or possibly singlet oxygen). It is speculated that this complex immediately breaks apart into degradation products of lignin. Lignin, because of its aromatic nature, absorbs strongly in the ultraviolet region of the spectrum. The typical lignin absorption spectrum comprises a maximum at 205nm (nanometers), a less intense peak at 280nm, with less significant shoulders in the spectrum at 250, 300 and 360nm.

In reducing the present invention to practice, pulp was subjected to treatment with ozone carried in oxygen while being irradiated at the aforementioned frequencies of ultraviolet light. A 360 watt spectrophotometer was used as the source of ultraviolet. Samples of pulp weighing 0.1 gram each (oven dried basis) were irradiated in a closed chamber consisting of two glass cells for a period of two hours. The cells were partially covered with reflective foil so as to increase the energy available to the pulp. In the data which follows the reduction in K number (increase in brightness) is on the order of two, which -- given the low power of the spectrophotometer -- is considered to be significant and having the potential to be translated to pilot or commercial scale apparatus.

Sample	K Number
Ultreated pulp	18.324
Ozonated pulp	17.389
Ozonated and irradiated at	
205nm	15.044
250nm	15.278
280nm	15.672
300nm	15.586
360nm	15.789

At each of these wave lengths which are characteristic of the absorption spectrum of lignin, the ultraviolet radiation increased the effectiveness of the ozonation. As may be seen, light at 205nm had the greatest effect. While commercially available light sources for photoreactors do not generally emit a single wavelength, it will be sufficient if some of the light is at one or more of the more effective frequencies. Moreover, it is desirable to choose wavelengths at which cellulose does not absorb. By irradiating at absorption peaks characteristic to lignin and not to cellulose, the lignin can be made more susceptible to attack by ozone than the cellulose thus tending to cause the ozone to react preferentially with lignin and tending to cause less degradation of cellulose.

While the present invention has been described in terms of a laboratory reduction to practice, it will be appreciated by one of ordinary skill in the art having the benefit of the teachings contained herein that the invention as defined by the appended claims is applicable to various types of reaction vessels already known in the art and incorporated herein by reference. Accordingly, it is to be understood that various changes in the forms of the apparatus by which the invention is practiced may be resorted to without departing from the spirit and scope of the invention as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A process for bleaching lignocellulosic pulp with ozone wherein the improvement comprises irradiating said pulp with ultraviolet light while mixing an ozone bearing gas with the pulp.

2. The process in accordance with claim 1 wherein said ultraviolet light contains frequencies corresponding to the absorption peaks characteristic to lignin.

3. The process in accordance with claim 2 wherein the frequency of said ultraviolet light is in the range of 205nm to 360nm.

4. The process in accordance with claim 1 wherein the ultraviolet light is concentrated at a frequency of 205nm.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 83/00820

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[3]: D 21 C 9/10

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC[3]	C 01 B; C 02 F; D 21 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	US, A, 4008120 (J.E. CARLES et al.) 15 February 1977 see columns 1,2 --	1
Y	Tappi J. Techn. Ass. Pulp Paper Ind., vol. 60, no. 9, September 1977 (Atlanta, GA, US) L.D. Markham et al. "The effect of ultraviolet light on the chlorine dioxide bleaching of kraft pulp", see pages 138-140 --	1-3
Y	US, A, 2161045 (W. HIRSCHKIND et al.) 6 June 1939 see the entire document --	1-3
Y	US, A, 4230571 (R.C. DADD) 28 October 1980 see columns 1,2 --	1-3
Y	US, A, 3920547 (R.L. GARRISON et al.) 18 November 1975 see figure; column 2, line 45 -	1 ./.

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
27th September 1983	20 OCT. 1983
International Searching Authority [1]	**Signature of Authorized Officer [20]**
EUROPEAN PATENT OFFICE	G.L.M. Kruijsenberg

Form PCT/ISA/210 (second sheet) (October 1981)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No [18]
	column 6, line 3 --	
A	Chemical Abstracts, vol. 96, no. 22, 31 May 1982 (Columbus, Ohio, US) K.D. Mgaloblishvili et al.: "Device for ozone decomposition", see page 160, left-hand column, abstract no. 183687d, SU, A, 895923, 7 January 1982 --	4
A	US, A, 3806404 (N. LIEBERGOTT et al.) 23 April 1974 see the entire document ------	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/US 83/00820 (SA 5482)

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 13/10/83

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 4008120	15/02/77	BE-A-	823480	16/04/75
		FR-A,B	2255418	18/07/75
		CA-A-	1040809	24/10/78
		SE-A-	7416010	23/06/75
US-A- 2161045		US-H-	T989185	
US-A- 4230571	28/10/80	None		
US-A- 3920547	18/11/75	None		
US-A- 3806404	23/04/74	FR-A,B	2186572	11/01/74
		DE-A,C	2327407	13/12/73
		AU-A-	5621473	28/11/74
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		JP-A-	49066902	28/06/74
		SE-B-	396970	10/10/77